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Calculation methods for the physical properties of air used in the calibration of microphones

A proposal for a unified calculation procedure to be used among European metrology laboratories

by

Knud Rasmussen

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DEPARTMENT OF ACOUSTIC TECHNOLOGY TECHNICAL UNIVERSITY OF DENMARK

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Preface

First revision April 1996. Report PL-11a.

In the original report the calculation of the density of humid air was based on the paper by P. Giacomo [2]. The first revision introduces the improvements adopted by CIPM in 1991 and reported in [3].

Second revision May 1997. Report PL-11b.

A personal communication with A. Zuckerwar revealed that the use of the Eucken relation for calculating the thermal diffusivity of air was too simplified. Although a more accurate determination of the diffusivity will not influence the final objective of the report, viz. the result of the calculation procedure used when calibrating microphones, the author decided - for the sake of completeness - to base the calculation of the thermal diffusivity on the fundamental definition. This involves a determination of the specific heat capacity C_p and the thermal conductivity k_a . As no method was found in the literature for calculating C_p for humid air an annex B is added, describing the derivation of C_p .

Calculation methods for the physical properties of air used in the calibration of microphones

A proposal for a unified calculation procedure to be used among European metrology laboratories

It is suggested that a mutual agreement be obtained among the European metrology laboratories on the procedure used to determine the acoustic properties of humid air when calibrating microphones and reporting the results. A unification of this procedure will ease the comparison of calibration results among the various laboratories. The present report refers the background and presents a proposal for these procedures.

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Calculation methods for the physical properties of air used in the calibration of microphones

Primary calibration of microphones are generally performed utilizing the reciprocity calibration technique. When calculating the sensitivities of the microphones, values for the gas properties play an important role in the calculation procedure. The gas quantities in question are the density, speed of sound, ratio of specific heats, viscosity and thermal diffusivity. All these quantities depends on one or more of the environmental conditions, viz. static pressure, temperature and relative humidity. Various values and calculation procedures can be found in the literature for these gas properties, out of which values for ordinary air under normal laboratory conditions are the most important.

The state of art in reciprocity calibration of microphones has reached a level where the influence on the calculated sensitivity of the measurement uncertainty and the stability of the microphones are of the same order of magnitude as the influence observed by using different values for the gas properties. Thus it is imperative that mutual agreement is obtained on how to derive the values for the relevant gas properties, in order that calibration results can be exchanged and compared in a well defined way.

This report reviews some of the latest results reported in the literature and which have found general international acceptance for instance through implementation in international standards. Based on this review, specific procedures are recommended for calculating each of the relevant gas properties. 2

Terminology

Throughout this proposal the following notation will be used for the various relevant gas quantities:

The quantities measured during the calibration are:

$p_{\rm s}$	static pressure
t	Celsius temperature
Н	percentage relative humidity

and the gas quantities to be calculated are:

ρ	density
С	speed of sound
$\kappa = c_p / c_V$	ratio of specific heats
η	dynamic viscosity
α_{t}	thermal diffusivity
α	the attenuation coefficient of sound in air

These quantities further requires a calculation of other variables, such as

x _c	mole fraction of carbon dioxide
$p_{\rm sat}$	saturation water vapor pressure
$f(p_{\rm s},t)$	enhancement factor
X _v	mole fraction of water vapour
Ζ	compressibility factor
Т	the absolute temperature
C_p	specific heat capacity at constant pressure
k _a	thermal conductivity
$f_{\rm rO}, f_{\rm rN}$	relaxation frequencies for oxygen and nitrogen
$\alpha_{\rm vO}, \alpha_{\rm vN}$	attenuation coefficients for vibrational relaxation in oxygen and
	nitrogen

Survey of relevant literature

The complete list of papers and reports dealing with determinations of values of the gas properties is tremendously long and shall not be reported here. Only a few papers and reports from the last 15 years selected by the author will be mentioned. Consequently some readers may find this report coloured by the authors personal preferences.

The major purpose of this investigations is to secure a unification of the procedures used to calculate the gas properties relevant for a reciprocity calibration of microphones. The procedure should be based on international recommendations or standards and on well documented theoretical and experimental work, in order that the procedure can be accepted by metrology laboratories as well as by the various national accreditation bodies.

The present international standard IEC 1094-2, 1992 [1] on pressure reciprocity calibration of microphones contains an informative Annex F describing the physical properties of air. However, the description is based on the assumption that moist air behaves as an ideal composite gas. Consequently the well-known relation

$$\rho c^2 = \kappa p_{\rm s} \tag{1}$$

between the variables are valid and only the density ρ and the speed of sound *c* need to be calculated while κ is determined through eq. (1). The determination of these quantities only consider the effects of humidity (water vapour) on the resulting molar mass of the composite gas. Further the reference value of the speed of sound in dry air at 0 °C is not unambiguously stated. Combined with the fact that the annex is only informative the calculated pressure sensitivities arising from a reciprocity calibration may differ by more than 0,03 dB depending on the method chosen for determining the gas properties.

In a discussion of a more concise calculation procedure it should also be taken into account that humid air is <u>not</u> an ideal gas. The most important consequence is that the above relation (1) is no longer valid and thus also the ratio of specific heats κ shall be calculated separately.

Although the calculation procedures become more complex for a non-ideal gas the complexity is of no practical importance with the available computer technique, even a

normal spreadsheet program is capable of performing the necessary calculations. The difference in the resulting calculated sensitivities between considering the gas to be ideal and non-ideal is in the order of 0,003 dB.

The present proposal for a unified calculation procedure is based on a non-ideal gas.

Density of moist air

The density of moist air plays an important role in mass metrology, due to the effect of air buoyancy when comparing two mass standards of different volume. Consequently this quantity has been studied very carefully and because the uncertainties in mass calibrations are several order of magnitudes smaller than in acoustics the method used in mass metrology for calculating the density should be adopted directly in acoustic metrology. The basic method has been approved by the International Committee for Weights and Measures (CIPM) and is reported in Metrologia by P. Giacomo [2]. It is often referred to as the CIPM-81 equation in order to indicate the year of its approval (1981). Later investigations have resulted in a more reliable value of the molar gas constant as well as an updating of some of the additional constant parameters entering the 1981-equation. These amendments have been adopted by CIPM in 1991 and are reported in [3]. The new equation is referred to as CIPM-81/91 and is the equation used in this report.

Note: The equation reported for calculating the water vapor saturation pressure differs from that recently adopted by ISO [15]. However the results are mutually in agreement within 0,1% in the range relevant for calibration of microphones and thus any of the expressions may be used.

Speed of sound in dry and moist air

The literature dealing with values for the speed of sound under various conditions can be divided into two groups. The first group deals with experimental results and the second group with numerical methods of calculating the zero-frequency sound speed in air under varying atmospheric conditions.

Most of the experimental work took place before 1970 and the generally accepted value for the speed of sound at 0 °C in dry air was $c_0 = 331,45$ m/s. The latest experimental results reported probably is by Giacobbe in 1993 [4]. Although the results by Giacobbe [4]

indicated a value of $c_0 = 331,5$ m/s for dry, CO₂ free air, this does not conflict with the previously accepted value, when the uncertainties in the measurements are taken into account. Wong [6] gives a list of reported sound speed investigations in the period 1919 to 1963. A plain average of 29 of the reported results gives a value of 331,52 m/s, neglecting all open air measurements and without performing any weighting of the findings according to the estimated measuring accuracy. The corresponding standard deviation is 0,18 m/s and thus the generally accepted value of 331,45 m/s is still valid.

The second group of papers deals with theoretical predictions of the speed of sound. Major contributions to this field are given by Morfey and Howell [7,9], Wong [6,10,11], Cramer [12].

Apart from the work by Wong the other authors support a value of 331,45 m/s as the zero-frequency sound speed for dry and CO₂ free air. The papers by Wong resulted in a heavy discussion [8,9,13 et.al] which at least put some light on the interpretation of earlier papers. The conclusion at the moment is that 'old' value of 331,45 m/s appears to be supported by a large majority of authors. A set of equations used to calculate the speed of sound at actual environmental conditions are given by Wong [10] and Cramer [12]. The two approaches are very similar but Wong's results refer to a static pressure of 101,325 kPa only and consequently do not show any dependency of this parameter. Since the static pressure is normally not under control during a calibration it is recommended to use the methods outlined by Cramer [12] to determine the zero-frequency speed of sound.

The speed of sound at the actual measurement frequency will differ from the zero-frequency value due to dispersion. For small values of the air attenuation, which will be the prevailing condition in a free-field reciprocity calibration of microphones, the effect of dispersion can be calculated from the expression [7,9]

$$\frac{1}{c_0} - \frac{1}{c_\phi} = \sum_n \frac{\alpha_{\nu n}}{2\pi f_{\nu n}} \tag{2}$$

where c_0 and c_{ϕ} are the zero-frequency- and the actual frequency speed of sound. α_v and f_v are the attenuation coefficient and relaxation frequency related to oxygen and nitrogen resp. These values are calculated from ISO 9613-1, 1993 [15]. Obviously the right side of the expression is a positive number and consequently the zero-frequency speed of sound will be lower than the actual speed of sound. At 20 kHz the difference is about 0,12% and thus the influence on the resulting microphone sensitivity is rather small.

NOTE: In IEC 1094-2, 1992 [1] a factor Δ is introduced, allegedly to compensate for the effect of dispersion. This is, however, a misinterpretation of the literature quoted. In [1] the speed of sound in moist air is calculated by taken only the change in molar mass of the gas into account. In order to compensate for the remaining effects (enhancement factor, compressibility, second order effects as well the mutual effects of the variables) the factor Δ is introduced as a constant in order to obtain the zero-frequency speed of sound. Thus the effect of Δ is actually to obtain the zero-frequency speed of sound for a non-ideal gas from the simplified expression given for an ideal gas rather than to compensate for dispersion effects. Furthermore a more correct value of Δ would be 0,99986.

Ratio of specific heats of air

The determination of values for the specific heat ratio is discussed by Wong [11,14] and Cramer [12]. For the same reason as above (the lack of the static pressure dependence in Wong's approach) it is recommended to follow the procedure given by Cramer [12].

Dynamic viscosity of air

The viscosity of air enters the calculations through the determination of the capillary tube impedance, the effect of heat conduction and the air attenuation coefficient, ie in correction terms to the main calculations. It is therefore not imperative to have a high accuracy on this quantity and in IEC 1094-2 [1] only a constant value is given. The viscosity depends slightly on temperature and humidity and [16] contains a reference to a fairly simple expression (eq. 11), which is recommended for the present purpose. (A different expression is given in [17] eq. 16).

Thermal diffusivity of air

The diffusivity of air also enters the calculations through the expressions for capillary tube impedance and heat conduction effects. As for the viscosity, a high accuracy is not important and IEC 1094-2 [1] recommends to use the Eucken relation. However, this relation is a crude approximation and for the sake of completeness the calculation of the thermal diffusivity shall be based on the basic definition

$$\alpha_{\rm t} = \frac{k_{\rm a}}{\rho C_p} \tag{3}$$

where k_a is the thermal conductivity and C_p the heat capacity of air at constant pressure both of which depends on temperature, static pressure and humidity.

Zuckerwar [16] refers a fairly simple expression for the thermal conductivity (eq. 12), which is also recommended here. The author has not been able to find similar expressions for the specific heat capacity in recent literature and thus annex B gives a detailed analysis on the derivation of the specific heat capacity for humid air.

Attenuation of sound in air

The attenuation of sound is an important factor in free-field reciprocity calibration of microphones. A very comprehensive work has been carried out before issuing ISO 9613-1 [15]. It is recommended to follow the calculation procedure laid down in [15] as also recommended in IEC 1094-3 [18].

Conclusion

The literature survey discussed above results in the following recommendations:

- 1) the density of air shall be calculated according to the CIPM-89/91 equation [2,3].
- 2) the ratio of specific heats and the zero-frequency speed of sound shall be calculated according to Cramer [12]
- 3) the attenuation of sound in air shall be calculated in accordance with ISO 9613-1 [15]
- 4) the dynamic viscosity of air shall be calculated according to Zuckerwar/Mason[16]
- 5) the diffusivity of air shall be calculated from the basic relation using the thermal conductivity calculated according to Zuckerwar/Mason [16] and the specific heat capacity at constant pressure as derived in annex B.
- 6) The effect of dispersion shall be calculated according to Howell and Morfey [7,9]. Annex A contains the complete equations necessary for these calculations.

The adoption of the above recommendation raises the question about where and when to use the quantities κp_s and ρc^2 in the expressions used to determine the resulting sensitivities of microphones in a reciprocity calibration.

In a free-field calibration only the values of ρ an *c* enter the expression for the acoustical transfer impedance and *c* is the speed of sound c_{ϕ} at the actual frequency.

In a pressure reciprocity calibration it can hardly be disputed that the calculated value of κ shall be used when determining the heat conduction correction and the impedance of the capillary tubes. It is, however, not immediately evident whether κp_s or ρc^2 shall be used in the expressions for the compliance of the coupler cavity or of the front cavity respectively equivalent volume of the microphones. In the derivation of the acoustical compliance of a cavity the equation of state of the gas enters and it can be given either as an explicit equation relating ρ , p and T, or in terms of the partial derivatives, assuming density ρ as a function of p and T. Basically the speed of sound as well as the ratio of the specific heats κ are derived from these partial derivatives (compressibilities under various conditions) and the density of the gas which indicates a preference for using the expression ρc^2 . On the other hand the largest difference between the two expressions will not exceed 0,5% within the environmental conditions prevailing under laboratory conditions (15 - 35 °C, 30 - 70 %RH, 85 - 105 kPa and frequencies below 30 kHz). For calibrations using a Plane Wave coupler this difference cannot be detected. For Large Volume couplers the frequency range is limited and the difference will only exceed 0,1% under extreme conditions.

In summary it is not important which of the above expressions is used during the calculations.

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ANNEX A

Procedures for calculating certain gas quantities

The equations given below are based on the following measured quantities:

- $p_{\rm s}$ static pressure in Pa t temperature in °C
- *H* relative humidity in %

Note the units of these quantities!

and

The quantities calculated, referring to the above measured environmental conditions are:

ho	density of air in kg/m ³
Co	zero-frequency speed of sound in m/s
c_{ϕ}	speed of sound at actual frequency in m/s
К	ratio of specific heats
η	viscosity of air in Pa·s
$\boldsymbol{\alpha}_{\mathrm{t}}$	diffusivity of air in m ² /s
α	air attenuation coefficient in Np/m.

During the calculations the following notation is used:

Т	$= T_{o} + t$, the thermodynamic temperature in K
T _o	= 273,15 K (0 °C)
T_{20}	= 293,15 K (20 °C)
$p_{\rm s,r}$	= 101325 Pa, the reference static pressure
$p_{\rm sv}(t)$	saturation water vapor pressure in Pa
$x_{\rm w}$	mole fraction of water vapor in air
x _c	mole fraction of CO ₂ in air
$f(p_{s},t)$	enhancement factor
Ζ	compressibility factor for humid air
k _a	thermal conductivity in cal/g
C_p	specific heat capacity at constant pressure in cal/g/K

relaxation frequency of oxygen
relaxation frequency of nitrogen
attenuation coefficients for vibrational relaxation in oxygen
attenuation coefficients for vibrational relaxation in nitrogen

Note that the units of k_a and C_p are given in cal/g and cal/g/K resp. To obtain the values in SI-units a conversion factor of 1 cal = 4.1868 J may be used.

The expressions for calculating the above quantities has been rewritten in order to use the same notation. The original references are shown for each equation. Further, a unified notation has been adopted for the various constants entering the expressions. The values of these constants are given in table A.1.

		Table A.1	- Coefficients	used in the eq	uations for g	gas quantities		
Coef-	Saturation water	Enhance-	Compressibility	Zero-frequency	Ratio of	Viscosity	Thermal	Specific heat
ficients	vapor pressure	ment factor		speed of sound	specific heats		conductivity	capacity at
								constant pressure
	$p_{ m sv}$	$f(p_{\rm s},t)$	Ζ	$c_{_0}$	К	η	$k_{ m a}$	C_p
a_{0}	1,237 884 7 \times 10 ⁻⁵	1,000 62	1,581 23×10 ⁻⁶	331,502 4	1,400 822	84,986	60,054	0,251 625
a_1	-1,912 131 6×10 ⁻²	$3,14{\times}10^{-8}$	-2,933 1×10^{-8}	0,603 055	$-1,75 \times 10^{-5}$	7,0	1,846	-9,252 5×10 ⁻⁵
a_2	33,937 110 47	$5,6\times10^{-7}$	$1,104.3 \times 10^{-10}$	-0,000 528	$-1,73 \times 10^{-7}$	113,157	$2,06 \times 10^{-6}$	2,133 4×10^{-7}
a_3	-6,343 164 5×10 ³		$5,707 \times 10^{-6}$	51,471 935	-0,087 362 9	-1	40	$-1,004 3 \times 10^{-10}$
a_4			$-2,051 \times 10^{-8}$	0,149 5874	-0,000 166 5	$-3,750 \ 1 \times 10^{-3}$	-1,775×10 ⁻⁴	0,124 77
a_5			$1,989 8 \times 10^{-4}$	-0,000 782	$-3,26 \times 10^{-6}$	-100,015		$-2,283 \times 10^{-5}$
a_6			-2,376×10 ⁻⁶	$-1,82 \times 10^{-7}$	$2,047 \times 10^{-8}$			$1,267 \times 10^{-7}$
a_7			1,83×10 ⁻¹¹	$3,73 \times 10^{-8}$	$-1,26 \times 10^{-10}$			0,011 16
a_8			-0,765×10 ⁻⁸	$-2,93 \times 10^{-10}$	5,939×10 ⁻¹⁴			$4,61 \times 10^{-6}$
a_9				-85,209 31	-0,119 971 7			$1,74 \times 10^{-8}$
a_{10}				-0,228 525	-0,000 869 3			
a_{11}				$5,91 \times 10^{-5}$	1.979×10 ⁻⁶			
a_{12}				-2,835 149	-0,011 04			
a_{13}				$-2,15 \times 10^{-13}$	$-3,478 \times 10^{-16}$			
a_{14}				29,179 762	0,045 061 6			
a_{15}				0,000 486	$1,82{\times}10^{-6}$			

Equations of calculation

Saturation water vapor pressure

$$p_{\rm sv}(t) = \exp(a_0 T^2 + a_1 T + a_2 + a_3 T^{-1})$$
 ([2] eq. 22)

or

$$p_{\rm sv}(t) = p_{\rm s,r} \, 10^C$$
 where $C = 4,6151 - 6,834.6 \left(\frac{T_0 + 0,01}{T}\right)^{1,261}$ ([15] eqs. B2,B3)

Enhancement factor

$$f(p_{\rm s},t) = a_0 + a_1 p_{\rm s} + a_2 t^2$$
 ([2] eq. 23)

Mole fraction of water vapor in air

$$x_{\rm w} = \frac{H}{100} \frac{p_{\rm sv}(t)}{p_{\rm s}} f(p_{\rm s}, t)$$
 ([2] eq. 19)

Compressibility factor

$$Z = 1 - \frac{p_{\rm s}}{T} \left[a_0 + a_1 t + a_2 t^2 + (a_3 + a_4 t) x_{\rm w} + (a_5 + a_6 t) x_{\rm w}^2 \right] + \left(\frac{p_{\rm s}}{T} \right)^2 \left[a_7 + a_8 x_{\rm w}^2 \right]$$
([2] eq. 24)

Mole fraction of carbon-dioxide in air

The composition of standard air is based upon a CO_2 mole fraction of 0,000 314. It is generally accepted that under laboratory conditions a higher value is found and in the absence of actual measurements a value of $x_c = 0,000$ 4 is recommended [1].

Density of air

$$\rho = \left[3,483\,49 + 1,44(x_{\rm c} - 0,000\,4)\right] \times 10^{-3} \frac{p_{\rm s}}{ZT} (1 - 0,378\,0x_{\rm w}) \tag{[2,3] eq. 16}$$

Zero-frequency speed of sound in air

$$c_{0} = a_{0} + a_{1}t + a_{2}t^{2} + (a_{3} + a_{4}t + a_{5}t^{2})x_{w} + (a_{6} + a_{7}t + a_{8}t^{2})p_{s}$$

$$([12] eq. 15)$$

$$+ (a_{9} + a_{10}t + a_{11}t^{2})x_{c} + a_{12}x_{w}^{2} + a_{13}p_{s}^{2} + a_{14}x_{c}^{2} + a_{15}x_{w}p_{s}x_{c}$$

Ratio of specific heats

Viscosity of air

$$\eta = \left(a_0 + a_1 T + \left(a_2 + a_3 T\right) x_w + a_4 T^2 + a_5 x_w^2\right) \times 10^{-8}$$
([16] eq. 11)

Thermal conductivity

$$k_{\rm a} = \left(a_0 + a_1 T + a_2 T^2 + \left(a_3 + a_4 T\right) x_{\rm w}\right) \times 10^{-8}$$
 ([16] eq. 12)

Specific heat at constant pressure

$$C_{p} = a_{0} + a_{1}T + a_{2}T^{2} + a_{3}T^{3} + (a_{4} + a_{5}T + a_{6}T^{2})x_{w} + (a_{7} + a_{8}T + a_{9}T^{2})x_{w}^{2}$$
(Annex B eq. B.7)

Diffusivity of air

$$\alpha_{\rm t} = \frac{k_{\rm a}}{\rho C_p}$$

Relaxation frequency of oxygen

$$f_{\rm rO} = \frac{p_{\rm s}}{p_{\rm s,r}} \left[24 + 4,04 \times 10^6 x_{\rm w} \left(\frac{0,2 + 10^3 x_{\rm w}}{3,91 + 10^3 x_{\rm w}} \right) \right]$$
([15] eq. 3)

Relaxation frequency of nitrogen

$$f_{\rm rN} = \frac{p_{\rm s}}{p_{\rm s,r}} \left(\frac{T}{T_{20}}\right)^{-\frac{1}{2}} \left[9 + 28,0 \times 10^3 x_{\rm w} \exp\left(-4,170 \left(\left(\frac{T}{T_{20}}\right)^{-\frac{1}{3}} - 1\right)\right)\right]$$
([15] eq. 4)

Attenuation coefficient of relaxation in oxygen in Np/m

/

$$\alpha_{\rm vO} = \frac{0,209 \cdot 2\pi}{35} \left(\frac{f/f_{\rm rO}}{1 + (f/f_{\rm rO})^2} \right) \frac{2f}{c} \left(\frac{2\,239,1}{T} \right)^2 \, \exp(-2\,239,1/T) \quad ([15] \,\text{Annex A})$$

where the speed of sound *c* ideally should be taken as the zero-frequency speed of sound. However for the present purpose it is sufficient to use the basic relation ([15] eq. A.5) $c = 331,45 \sqrt{T/T_0} = 343,37 \sqrt{T/T_{20}}$. Thus the above equation reduces to

$$\alpha_{\rm vO} = 0.012\,75 f^2 \left(\frac{\exp(-2\,239.1\,/\,T)}{f_{\rm rO} + f^2\,/\,f_{\rm rO}}\right) \left(\frac{T_{20}}{T}\right)^{\frac{5}{2}}$$

Attenuation coefficient of relaxation in nitrogen in Np/m

$$\alpha_{\rm vN} = \frac{0.781 \cdot 2\pi}{35} \left(\frac{f/f_{\rm rN}}{1 + (f/f_{\rm rN})^2} \right) \frac{2f}{c} \left(\frac{3\,352.0}{T} \right)^2 \, \exp(-3\,352.0\,/\,T) \qquad ([15] \,\text{Annex A})$$

or

$$\alpha_{\rm vN} = 0,106 \ 8f^2 \left(\frac{\exp(-3\ 352,0\ /\ T)}{f_{\rm rN} + f^2\ /\ f_{\rm rN}}\right) \left(\frac{T_{20}}{T}\right)^{\frac{5}{2}}$$

Speed of sound at actual frequency

1	_ 1	$\alpha_{\rm vO}$	$\alpha_{ m vN}$	([7] o
c_{ϕ}	$\overline{c_0}$	$\frac{1}{2\pi f_{\rm rO}}$	$2\pi f_{\rm rN}$	

16

Air attenuation coefficient in Np/m

$$\alpha = 18,4 \times 10^{-12} f^2 \left(\frac{p_{\rm s}}{p_{\rm s,r}}\right)^{-1} \left(\frac{T}{T_{20}}\right)^{\frac{1}{2}} + \alpha_{\rm vO} + \alpha_{\rm vN}$$
([15] eq. 5)

or

$$\alpha = f^2 \left[18,4 \times 10^{-12} \left(\frac{p_{\rm s}}{p_{\rm s,r}} \right)^{-1} \left(\frac{T}{T_{20}} \right)^{\frac{1}{2}} + \left(\frac{T}{T_{20}} \right)^{-\frac{5}{2}} \left(0,01275 \frac{\exp(-2239,1/T)}{f_{\rm rO} + f^2/f_{\rm rO}} + 0,1068 \frac{\exp(-3352,0/T)}{f_{\rm rN} + f^2/f_{\rm rN}} \right) \right]$$

ANNEX B

Procedure for calculation of C_p for humid air.

The general rule for calculating the resulting value of the heat capacity at constant pressure C_p for a mixture of two gases such as dry air and water vapour is:

$$C_p = C_{p,a} \frac{x_a M_a}{M} + C_{p,w} \frac{x_w M_w}{M}$$
(B-1)

where index a and w denotes air and water resp. M and x is the molar mass and the mole fraction of the indexed component.

The heat capacity is a function of temperature and can generally be written as:

$$C_{p,i} = c_0 + c_1 T + c_2 T^2 + c_3 T^3 = \sum_{k=0}^{3} c_{k,i} T^k$$
(B-2)

where the coefficients c_k depends on the actual gas considered.

Air in itself is a mixture of various gases and is generally described by a standard composition (ISO 2533) of the single gases. The resulting heat capacity for dry standard air is determined by the general rule given by eq. B-1 combined with eq. B-2.

$$C_{p,a} = \sum_{i} C_{p,i} \frac{x_i M_i}{M} = \sum_{k=0}^{3} \frac{\sum_{i=0}^{3} c_{k,i} x_i M_i}{M} T^k = \sum_{k=0}^{3} b_k T^k$$
(B-3)

Table B.1 shows the above coefficients for the single components of dry air. The table shows the molar mass and mole fraction of the single gas components for dry standard air, except that the content of carbon dioxide has been increased to 0,04%. In consequence the contribution x_iM_i of the individual gas components are corrected to correspond to $\sum x_i = 1$. Where possible the coefficients refer to real gases cf. ref. [19,20].

The final expression for determining C_p in cal/g/K for dry air then will be:

$$C_{p,a} = 0.251\ 625 - 9.252\ 5 \cdot 10^{-5}\ T + 2.133\ 4 \cdot 10^{-7}\ T^2 - 1.004\ 3 \cdot 10^{-10}\ T^3 \quad (B-4)$$

For water vapour a similar expression holds ([20] eq. A8),

$$C_{p,w} = 0.452\ 219 - 1.292\ 24 \cdot 10^{-4}\ T + 4.170\ 08 \cdot 10^{-7}\ T^2 - 2.004\ 01 \cdot 10^{-10}\ T^3 \qquad (B-5)$$

although these data refer to an ideal gas.

The resulting heat capacity for the mixture of dry air and water vapour is then determined from eq. B-1.

Having in mind that

$$x_{a} + x_{w} = 1,$$

$$M = x_{a} M_{a} + x_{w} M_{w}$$

and $M_{\rm w}/M_{\rm a} = 0,622$

eq. B-1 can be rewritten into

$$\begin{split} C_p &= \frac{C_{p,\mathrm{a}} + x_\mathrm{w}(0.622 \ C_{p,\mathrm{w}} - C_{p,\mathrm{a}})}{1 - 0.378 \ x_\mathrm{w}} \\ &\approx \left(C_{p,\mathrm{a}} + x_\mathrm{w}(0.622 \ C_{p,\mathrm{w}} - C_{p,\mathrm{a}}) \right) \cdot (1 + 0.378 \ x_\mathrm{w}) \\ &= C_{p,\mathrm{a}} + x_\mathrm{w} \cdot 0.622 \ (C_{p,\mathrm{w}} - C_{p,\mathrm{a}}) + x_\mathrm{w}^2 \ (0.235 \ C_{p,\mathrm{w}} - 0.378 \ C_{p,\mathrm{a}}) \end{split} \tag{B-6}$$

where the last expression is brought into the same form as the expressions for the other variables for the acoustic properties of humid air.

Neglecting two higher order terms, the last expression can be rewritten and ten new coefficients $a_0 - a_9$ be defined. C_p is then given by

$$\begin{split} C_p &= a_0 + a_1 T + a_2 T^2 + a_3 T^3 \\ &+ (a_4 + a_5 T + a_6 T^2) \, x_{\rm w} \\ &+ (a_7 + a_8 T + a_9 T^2) \, x_{\rm w}^2 \end{split} \tag{B-7}$$

The ten coefficients are derived from the data in Table B.1 and are listed in Table A.1.

Note that the results will be in units of cal/g/K. However, the value of C_p is used only for calculating the diffusivity α_t given by eq. 3, where k_a , the thermal conductivity, is given in cal/g. The ratio k_a/C_p will then be in SI-units and no further conversion is necessary.

Gas	Molar mass	Mole			afficiants c	an B_7) see [10	100		R aculting coaf	ficiants (ad B_3	
	g/mol	fraction	g/mol	5		(1) vve (2-4. pv	ر٥4,		TOOL BIIIII COOL	a .py) emoran	
	M_i	x_i	$x_i^*M_i/\operatorname{sum}(x_i)$	c_0	c_1	c_2	c_{3}	b_0	b_1	b_2	b_3
N_2	28,013 4	0,780 84	21,872 15	0,261 365	$-9,01 \times 10^{-5}$	$1,80 \times 10^{-7}$	-7,09×10 ⁻¹¹	0,197 357	$-6,804 \times 10^{-5}$	$1,362 \times 10^{-7}$	$-5,354 \times 10^{-11}$
\mathbf{O}_2	31,998 8	0,209 476	6,702 42	0,227 218	$-1,06 \times 10^{-4}$	$3,33 \times 10^{-7}$	$-2,02 \times 10^{-10}$	0,052 576	$-2,462 \times 10^{-5}$	$7,714 \times 10^{-8}$	$-4,680 \times 10^{-11}$
Ar	39,948	0,009 34	0,373 083	0,124 522	0	0	0	0,001 604	0	0	0
CO_2	44,009 95	0,000 4	0,017 603	0,136 812	$2,15{\times}10^{-4}$	$7,25 \times 10^{-8}$	$-1,57 \times 10^{-10}$	$8,314 \times 10^{-5}$	$1,309 \times 10^{-7}$	$4,407{\times}10^{-11}$	$-9,550 \times 10^{-14}$
Ne	20,183	$1,82{\times}10^{-5}$	0,000 367	0,246 15	0	0	0	3.118×10^{-6}	0	0	0
Kr	83,8	$1,14{\times}10^{-6}$	9,552×10 ⁻⁵	0,059 284	0	0	0	$1,955 \times 10^{-7}$	0	0	0
CH_4	16,043 03	$2,0{\times}10^{-6}$	$3,208 \times 10^{-5}$	0,495 585	$-5,26 \times 10^{-4}$	$2,72{\times}10^{-6}$	-1,76×10 ⁻⁹	$5,489{\times}10^{-7}$	$-5,822 \times 10^{-10}$	$3,008 \times 10^{-12}$	$-1,954 \times 10^{-15}$
He	4,002 6	$5,24 \times 10^{-6}$	2,097×10 ⁻⁵	1,241 2	0	0	0	$8,987 \times 10^{-7}$	0	0	0
N_2O	44,012 8	$2,70{\times}10^{-7}$	$1,188 \times 10^{-5}$	0,103 451	$4,89{\times}10^{-4}$	-5,19×10 ⁻⁷	$2,45 \times 10^{-10}$	$4,244{\times}10^{-8}$	$2,007 \times 10^{-10}$	$-2,130{\times}10^{-13}$	$1,004 \times 10^{-16}$
Xe	131,3	$8,70{\times}10^{-8}$	$1,142 \times 10^{-5}$	0,037 837	0	0	0	$1,492{\times}10^{-8}$	0	0	0
CO	28,01	$1,90 \times 10^{-7}$	$5,321 \times 10^{-6}$	0,261 531	-9,32×10 ⁻⁵	$1,94 \times 10^{-7}$	-7,15×10 ⁻¹¹	$4,805{\times}10^{-8}$	$-1,713 \times 10^{-11}$	$3,555 \times 10^{-14}$	$-1,313 \times 10^{-17}$
H_2	2,0159 4	$5,00 \times 10^{-7}$	$1,008 \times 10^{-6}$	1,539 5	$1,51 \times 10^{-2}$	$-4,02 \times 10^{-5}$	$3,64{\times}10^{-8}$	$5,358 \times 10^{-8}$	$5,248 \times 10^{-10}$	$-1,400{\times}10^{-12}$	$1,265 \times 10^{-15}$
Sum	for dry air	1,000 084	28,965 81					0,251 625	$-9,252 5 \times 10^{-5}$	$2,133 4 \times 10^{-7}$	$-1,004$ 3×10^{-10}
Water	$M_{ m w}$										
vapour	18,01534			0,452 219	-1,292 2×10 ⁻⁴	$4,170~08{\times}10^{-7}$	$-2,004\ 01\!\times\!10^{-10}$	0,452 219	$-1,292 2 \times 10^{-4}$	$4,170\ 08 \times 10^{-7}$	-2,004 01×10 ⁻¹⁰

Table B.1 - Coefficients for gas constituents